We will take advantage of two properties to instead develop a statistical connection between microscopic & bulk properties

Ensemble method & ergodic hypothesis

Definitions (reminder)

Macrostate – thermodynamic state of the system eg N, V, E or N, V, T or n, p, T

Microstate – $\underbrace{x, y, z, p_x, p_y, p_z}_{\text{configuration of system, eg}}$ of every atom

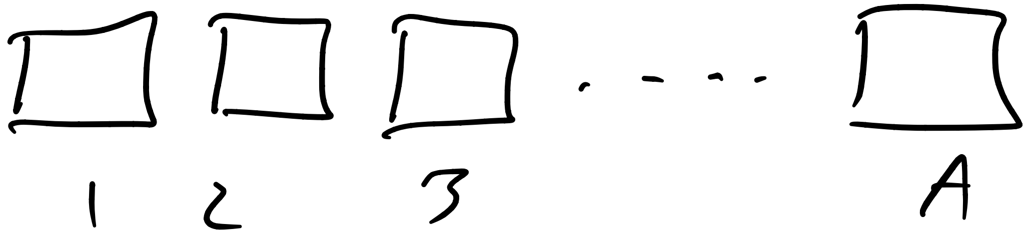
Ergodicity – long enough time, system explores all microstates

spends "correct" amount of time in each one (more later)

Ensemble method – if had many copies of system, average over copies gives same result as $t \to \infty$ of one copy } ergodic hypothesis

Suppose a system has M possible states

A total copies of system



let N_i be the number in state i

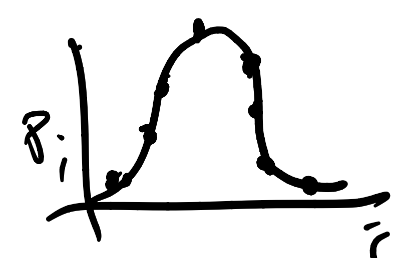
$$\sum_{i=1}^{M} N_i = A$$

$$\{N_i\} = \{N_1, N_2, \dots N_m\}$$

prob of each state 1 – m

$$\{P_i\} = \{P_1, \dots, P_m\} = \left\{\frac{N_1}{A}, \frac{N_2}{A}, \dots \frac{N_m}{A}\right\}$$

Ensemble average, of property y



$$\langle Y \rangle_{ens} = \frac{1}{M} \sum_{i=1}^{M} y_i P_i$$

Should be same as time avg $\langle y \rangle_t = \frac{1}{N_t} \sum_{j=1}^{N_t} y(t_j)$

An ensemble is a collection of copies of a system all in the same macrostate

A "microcanonical" ensemble is one with const N, V, E — isolated system obeying Newton's equations $F = ma$, conserve E

How often does each microstate occur?
equilibrium maximizes entropy!

$S = k_B \ln W$, but what is $W(N, V, E)$ for an ensemble

N_1 copies in state 1, N_2 copies in state 2, ...

$$\sum_{i=1}^{A} N_i = A$$

$$W = \frac{A!}{N_1! \, N_2! \, N_3! \cdots N_m!} \quad \text{(multinomial)}$$

for A & N_i large

$$S = k \ln W = A \ln A - A - \sum_{i=1}^{m} (N_i \ln N_i - \underbrace{N_i}_{\text{adds to } A})$$

so $S/k_B = A\ln A - A - \sum N_i \ln N_i$

$$\frac{1}{k_B}\frac{\partial S}{\partial N_i} = 0 \quad \text{for all } N_i$$

$$\frac{1}{k_B}\frac{\partial S}{\partial N_j} = \frac{\partial (A\ln A)}{\partial N_j} - \frac{\partial}{\partial N_j}\left(\sum_{i=1}^{m} N_i \ln N_i\right)$$

↑ only j matters

$$A = \sum_{i=1}^{m} N_i$$

$$\frac{1}{A}\frac{\partial A}{\partial N_j}$$

$$= A\frac{\partial \ln A}{\partial N_j} + \frac{\partial A}{\partial N_j}\ln A - \frac{N_j}{N_j} - \ln N_j$$

$$= 1 + \ln A - 1 - \ln N_j$$

$$= \ln A - \ln N_j$$

Smallest for N_j all maximized

But can't make all N_j max simultaneously

because $\sum N_j = m$, need a constraint

Turns out (see pg 312 - 313)

Lagrange Multipliers for constraint

Instead, find whed

$$I = f(x) - \alpha\,(\text{constraint}) \text{ is max}$$

$$I = k \ln \omega - \alpha \left(\sum_{i=1}^{m} N_i - A \right) = 0$$

$$\frac{\partial I}{\partial N_j} = \ln A - \ln N_j - \alpha = 0 \quad \forall N_j$$

$$\alpha = \ln (A/N_j) \text{ is a constant}$$

$$\frac{N_j}{A} = e^{-\alpha} \quad \forall N_j$$

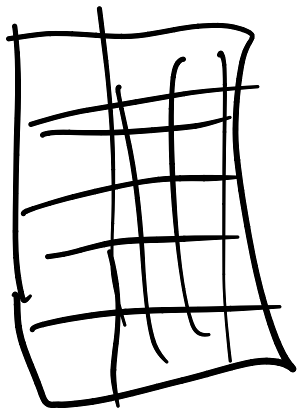
find λ by enforcing constraint

$$\sum N_j = A = \sum_{i=1}^{m} A e^{-\alpha} \Rightarrow e^{\alpha} = m$$

$$P_i = N_i / \sum N_i = \frac{1}{m} \text{ ? equal distribution!}$$

Chapter 10 - Canonical Ensemble

Consider bunch of copies of system



N, V, E overall

know heat transfer until have same temp

$S = k \ln W$

but Now

so for one system,

$\tilde{N}, \tilde{V}, T$

where $N = A\tilde{N}$ atom

$V = A\tilde{V}$

$$E = \sum_{i=1}^{m} E_i N_i$$

Max S w/ E constraint & $\sum N_i = A$ sum over states

$$S/k_B = \ln A - \alpha\left(\sum N_i - A\right) - \beta\left(\sum N_i \varepsilon_i - \varepsilon_T\right)$$

$$\frac{\partial S/k_B}{\partial N_j} = \ln \frac{A}{N_j} - \alpha - \beta \varepsilon_j = 0$$

and so $N_j = e^{-\alpha} e^{-\beta \varepsilon_j} \cdot A$

$$\sum_{j=1}^{m} N_j = A = A \sum_{j=1}^{m} e^{-\alpha} e^{-\beta \varepsilon_j}$$

so $e^{\alpha} = \sum_{j=1}^{m} e^{-\beta \varepsilon_j}$

this means $P_j = \frac{N_j}{A} = \frac{e^{-\beta \varepsilon_j}}{\sum_{j=1}^{m} e^{-\beta \varepsilon_j}}$ ★

$Q = \sum_{j=1}^{m} e^{-\beta \varepsilon_j}$ is "partition function"

for canonical ensemble & $e^{-\beta \varepsilon_j}$

is the Bolzmann factor (relative weight) for microcanonical ensemble

$\beta F = 1$ (like $\varepsilon_j = 0 \ \forall j$ or $\beta = 0$)

and $Q = \sum \beta F_i = \sum 1 = m$

Average of y

$$\langle y \rangle = \sum_{i=1}^{m} y_i P_i = \sum_{i=1}^{m} y_i e^{-\beta\varepsilon_i} / Q$$

Eg $$\langle \varepsilon \rangle = \sum_{i=1}^{m} \varepsilon_i e^{-\beta\varepsilon_i} / Q$$

Turns out / can show by connection to classical thermo that

$$\beta = 1/k_B T$$

so $$Q = \sum_{i=1}^{m} e^{-\varepsilon_i / k_B T}$$ ← can get other thermo quantities from this function

$$\frac{\partial \ln x}{\partial \beta} = \frac{1}{x}\frac{\partial x}{\partial \beta}$$ if we consider

$$-\frac{\partial \ln Q}{\partial \beta} = \frac{-1}{Q}\frac{\partial Q}{\partial \beta} = \frac{1}{Q}\sum_{i=1}^{m} \varepsilon_i e^{-\beta\varepsilon_i}$$

$$U = -\frac{\partial \ln Q}{\partial \beta}$$

also $$\frac{\partial f}{\partial \beta} = \frac{\partial f}{\partial T}\frac{\partial T}{\partial \beta} = \frac{\partial f}{\partial T}\left(\frac{\partial \beta}{\partial T}\right)^{-1}$$

$$= -\left(\frac{1}{k_B T^2}\right)^{-1}\frac{\partial f}{\partial T}$$

so $$U = k_B T^2 \frac{\partial \ln Q}{\partial T}$$

Gibbs Entropy

$$S = -k_B \sum p_i \ln p_i$$

$$= -k_B \sum_i p_i \left[-\beta \varepsilon_i - \ln Q\right]$$

$$= k_B \beta \sum_i p_i \varepsilon_i + \ln Q$$

$$= k_B \beta + k_B \ln Q$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V = \frac{\left(\frac{\partial U}{\partial \beta}\right)_V}{\left(\frac{\partial S}{\partial \beta}\right)_V}$$

$$\frac{\partial S}{\partial \beta} = k_B\left(U + \beta \frac{\partial U}{\partial \beta} + \underbrace{\left(\frac{\partial \ln Q}{\partial \beta}\right)}_{-U}\right)$$

$$= k_B \beta \left(\frac{\partial U}{\partial \beta}\right)_V$$

so $T = \dfrac{1}{k_B \beta} \Rightarrow \beta = \dfrac{1}{k_B T}\,\cancel{A}\,!$